

ANODE SPOTS AND THEIR RELATIONS TO THE ABSORPTION AND
EMISSION OF GASES BY THE ELECTRODES
OF A GEISSLER DISCHARGE

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
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BY

CHARLES HASTINGS THOMAS

Reprinted from *PHYSICAL REVIEW*, pp. 72-91, Vol. 35, No. 1, January 1, 1930

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ABSTRACT

In a Geissler discharge containing H_2 , N_2 , CO , mixtures of hydrogen and the rare gases or mixtures of mercury vapor in the rare gases at pressures of 0.5 to 12 mm and electrode separation of 4 to 30 cm, the anode glow breaks up into a number of bright hemispherical spots, more or less symmetrically arranged when the polarity of a direct current discharge is reversed. Anode spots do not form in O_2 , A or Ne but faint spots form in He which contain a trace of H_2 . It is shown that one necessary condition for the formation of spots is the emission of gas from the surface of the anode. As many as 75 spots arranged in 5 concentric rings have been observed on an anode 34 mm in diameter. Conditions governing the number, size and duration of the spots have been determined. Spots formed on all the metals tried; Fe , Ni , Al , Cu , Hg and brass. The formation of anode spots has been used to prove that in a Geissler discharge between cold electrodes, the cathode absorbs gas and the anode emits gas at rates which are functions of the current density, gas pressure, kind of gas and electrode temperature. It is shown that the increase of the potential drop of a discharge with time, is due almost wholly to an increase in the gas content of the cathode, and that the potential drop immediately after starting a discharge is lowered by previously degassing the cathode by means of an induction furnace or by using this electrode as anode.

INTRODUCTION

ALTHOUGH hundreds of investigations have been carried out during the past fifty years on some part or other of the Geissler discharge, a complete understanding of the phenomena which occur therein is still lacking. Among these phenomena is the "clean up" or disappearance of the gas. It has long since been postulated that the electrodes absorb gas but in the past no direct proof of this has been given although the several explanations^{1,2,3,4} of the phenomena of cathode sputtering have as their bases the absorption of gas by the cathode or the existence of gas in it.

That certain gases diffuse through certain metals is shown by the diffusion of hydrogen through palladium. Yamada⁵ has shown by spectroscopic analysis that absorption of hydrogen in palladium produced a uniform expansion of the space lattices by 2.9 percent. He found no evidence that the absorbed hydrogen had reacted with the palladium.

¹ Hittorf, Wied. Ann. **21**, 126 (1884).

² Kingdon and Langmuir, Phys. Rev. **22**, 148 (1922).

³ Berliner, Weid. Ann. **33**, 291 (1888).

⁴ Kohlschutter, Jahrb. d. Radioakt. **4**, 353 (1912).

⁵ Yamada, Phil. Mag. **45**, 241 (1923).



Baum⁶ has made microphotographs of silver cathodes which had been used in a Geissler discharge of 3000 volts in which he found that gas molecules had penetrated to a depth of 1.5 mm.

In some recent experiments, one of the writers has had occasion to investigate an alternating current Geissler discharge in hydrogen. He found that during one half of the cycle of alternating current the discharge did not strike. During the succeeding half cycle, the discharge struck when the voltage had attained the sparking potential of the gas for the existing pressure-distance conditions. A check on the history of these electrodes showed that they were of the same metal and that they had been subjected to the same treatment except that a direct current discharge in hydrogen had previously been passed between them. The discharge struck with A.C. when the electrode previously used as anode in the D.C. discharge was negative.

This experiment shows that the use of an electrode as anode or cathode changes its sparking potential. Later in this paper, it will be shown that this difference in sparking potential was due mainly to a difference in the amounts of gas absorbed in each electrode. During the investigation of this difference in sparking potential, the anode spots appeared. The term anode spots is used throughout this paper to apply to the hemispherical bright spots which were more or less symmetrically arranged on the cathode side of the anode.

The appearance of anode spots has been previously reported by Lehmann⁷ who found them in a discharge in air in a tube of wide diameter, and by Mackay⁸ who found more elaborate patterns in helium. Neither author attempted any explanation of the formation of the anode spots.

OBJECT

In the light of this information, it seemed advisable to make the following investigations: (1) A determination of the cause of anode spots; (2) A study of their characteristics; (3) An application of the phenomenon of anode spots to the study of emission and absorption of gases by the electrodes of a Geissler discharge; (4) A study of the effect of gas absorbed in the electrodes on the potential drop of the discharge.

APPARATUS

The vacuum system consisted of the usual pumps, mercury cut-off and liquid air trap. The gas pressure in the system was determined by means of two McLeod gauges whose combined range extended from 30 mm to 2×10^{-5} mm of mercury. A gas storage and purifying system was connected by suitable stopcocks to the vacuum system so that either all parts could be evacuated to a high degree or purified gas could be admitted to the experimental tube.

Figure 1 is a diagram of the experimental tube most used. The tube proper was 63 cm in length and 6 cm in diameter. Electrical connections were made

⁶ Baum, *Zeits. f. Physik* **40**, 690 (1926).

⁷ Lehmann, *Ann. d. Physik* **7**, 8 (1902).

⁸ Mackay, *Phys. Rev.* **15**, 309 (1920).

to the movable electrode through a capillary glass tubing which supported it. By means of a magnetic force on a cylinder of soft iron which was fastened to this capillary shaft, the one electrode could be moved through a distance of 30 cm. The electromagnet for moving this electrode was mounted on a screw device which permitted a slow regular movement of the electrode.

Electrodes of several sizes, shapes and thicknesses were used as well as similar electrodes with different degrees of polish. In several cases, extreme care was taken that no foreign material touched the electrode surface except the steel tool with which it was turned down. The electrodes were supported on glass stoppers in such a way that only one half inch of metal was exposed behind each electrode. Thus the distortion of the electric field was reduced to a minimum. The glass stoppers were ground to fit another tube of the same length as the first but of a diameter 4 cm larger than the latter. A third glass stopper which supported a spiral tungsten filament was interchangeable with the stopper which carried the fixed cold electrode.

A direct current motor-generator set supplied the potential which was regulated by changing the resistance in the circuit of the field exciter. The voltage across the tube was measured on a Jewell voltmeter of range 0 to 500

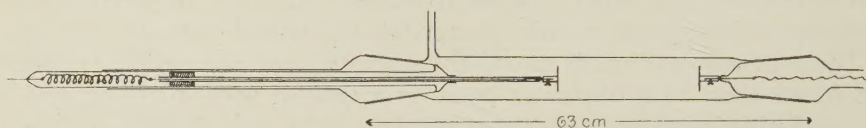


Fig. 1. Experimental tube.

volts. This voltmeter was equipped with suitable external resistances by means of which the voltage range could be extended up to 2000 volts. A resistance of 3000 ohms was placed in series with the experimental tube. By means of a reversing switch the direction of the discharge through the experimental tube was easily changed.

PROCEDURE

Whenever any appreciable sputtered material appeared on the inner walls of the tube or when a change of electrodes was made, the tube was disassembled and cleaned with aqua regia. Subsequently, the tube was mounted in its usual position and the glass stoppers were turned until the electrodes were parallel and symmetrically placed as judged by the eye after which the ground glass joints were sealed with De Khotinsky cement. The necessary precautions were taken for the removal of water vapor and occluded gases and for the exclusion of mercury vapor from the tube.

Extreme care was exercised in order to obtain pure hydrogen, carbon monoxide, argon, neon and helium. However, in no case was it possible to remove all traces of hydrogen from helium, possibly because the system and tube had previously been used for hydrogen.

The electrode separation was determined by measuring the relative position of the soft iron cylinder on the shaft which supported the movable

electrode. By this method the electrode separation could be easily determined within one half a mm regardless of the condition of the discharge tube proper.

When the gas, tube, and electrodes were properly prepared, the gas was admitted slowly to the tube through a liquid air trap until the desired pressure was attained. In the cases in which the effects of complete degasification of electrodes were investigated, the discharge was set up in the tube within a few seconds after the gas was admitted to the tube in order that the electrodes might have little time for absorption of the gas.

The ordinary procedure was to allow the one electrode to serve as cathode for a given time at a given current. This is called the period of "soaking" during which the cathode absorbed gas through positive ion bombardment. The polarity of the electrodes was then reversed so that the electrode which had been soaked as cathode now became the anode. Anode spots then formed on the anode if the pressure-electrode distance conditions were suitable. The discharge was then maintained at a constant current or potential during the period of the existence of these spots on the anode.

As soon as the last spot disappeared from the anode, the discharge was stopped, since it is assumed that for a given current, the spots disappeared when the rate of evolution of the gas from the anode had decreased to a critical value. Within a few seconds after the discharge was stopped, as mentioned above, the process was repeated. Thus a series of observations which showed the effects of the soaking of the cathode on the characteristics of the anode spots were obtained.

It was observed early in this investigation that the number of spots which appeared under similar conditions of current, pressure, etc., was different depending on whether the current was increased or decreased in order to obtain the desired value. This was to be expected since the spots often formed in patterns such that a considerable change in current was necessary to change the pattern. It was necessary, therefore, to use the same applied potential difference at each closing of the switch in order to obtain consistent results in the number of spots which were formed on the anode.

Throughout the work, particular attention was paid only to the one electrode for which the gas content and previous treatment had to be known at all times.

Photographs were taken at an angle of 30 degrees with the axis of the tube. Sometimes difficulty was encountered in obtaining a satisfactorily stationary pattern. The photographs of the spots which are presented in the succeeding parts of this paper were obtained with an exposure of one-fifth second on a Voightlander camera which had an F 4.5 lens.

RESULTS

Presentation and discussion of photographs: The photographs presented in Figure 2 were chosen because they show the relative difference in the size of the spots. In pictures *a*, *b*, *c*, and *d*, the electrodes were 41 mm in diameter, while those in pictures *e*, *f*, *g*, and *h* were 34 mm in diameter. In picture *g*, the

spots were rotating rapidly under the influence of their own magnetic field. Picture *h* which was taken perpendicular to the axis of the tube shows the hemispherical form of the spots and their appearance back of a striation.

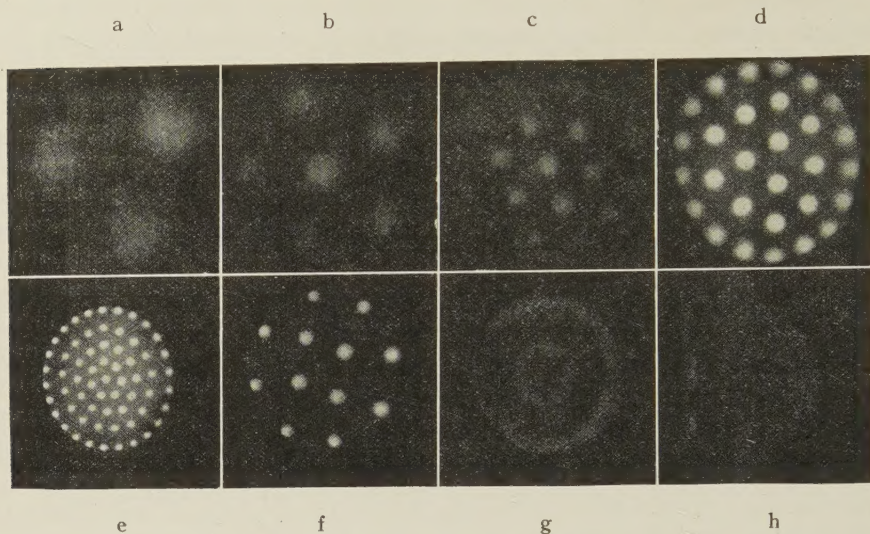


Fig. 2. Typical patterns of anode spots.

The experimental conditions for the patterns which are presented in Figure 2 are given in Table I.

TABLE I.

Pattern	Kind of gas	Gas pressure in mm Hg	Electrode separation in cm	Potential drop in volts	Current in milliamperes
<i>a</i>	nitrogen	0.41	10.5	825	17
<i>b</i>	hydrogen	2.25	16.9	880	125
<i>c</i>	hydrogen	5.8	12.3	625	275
<i>d</i>	hydrogen	3.3	14.7	881	180
<i>e</i>	(argon 90%) (hydrogen 10%)	9.0	10.8	690	240
<i>f</i>	hydrogen	3.1	13.2	920	160
<i>g</i>	hydrogen	3.35	14.3	1240	200
<i>h</i>	hydrogen	2.55	18.3	902	85

Results for different gases. Anode spots did not form in any gas when the electrodes had been sufficiently degassed provided that mercury vapor was excluded from the tube and that the discharge was set up within two minutes after the admission of the gas. In general, anode spots formed in hydrogen, nitrogen, carbon monoxide, air, and in certain gas mixtures. Spots did not form in oxygen, pure argon or pure neon. The formation of very weak spots in helium which contained a trace of hydrogen will be discussed later.

In a discharge in hydrogen, the spots formed over a gas pressure range of from 0.6 to 12 mm. The gas pressure limits varied with different gases; but in all gases, the lower pressure value was limited by the possible electrode separa-

tion and the higher pressure value was limited by the limit of the current which was available from the generator. Hydrogen was different from other gases in that, for a given pressure, the spots formed over a comparatively wide range of electrode separation which in some cases was as much as 20 cm. When striations were present in the hydrogen discharge, the spots appeared when the anode was placed in the dark space between the striations. The spots disappeared and reappeared as the anode was moved through the bright part and the dark part of the striations respectively. In case the configuration of spots was made up of several rings, the outside ring disappeared first as the anode was moved through a striation which, for the smaller electrodes, was conical in shape.

When a well-degassed electrode was allowed to remain in hydrogen for a few minutes, spots which lasted as long as a second or two were formed at the first passage of the discharge. This observation shows that the metal of the electrodes absorbed hydrogen even in the absence of an electric field. Degasification of the electrodes by means of the induction furnace after they had been used in hydrogen gas was almost as difficult as was the degasification of new electrodes.

The anode spots formed easily in nitrogen over a pressure range of 0.4 to 14 mm of mercury for available electrode separation and current limits. In nitrogen, however, the spots formed only at the beginning of the positive column within a range of two cm at most. As the anode was moved farther into the Faraday dark space, the spots gradually disappeared. When the anode was moved farther into the positive column, the configuration of spots became unstable and finally merged into the positive column. This peculiarity of limitation of the formation of spots to the neighborhood of the beginning of the positive column in nitrogen and other gases which gave a strong positive column make it impracticable to carry out as extensive investigations in these gases as in hydrogen.

Anode spots formed very readily when the anode was placed near the beginning of the positive column of a discharge in carbon monoxide. The spots which were greenish white in color in this gas, formed over a pressure range of 0.4 to 15 mm of mercury for the electrode separation and current limits of the apparatus. For a given period of "soaking" of the cathode in carbon monoxide, the spots lasted much longer than in either hydrogen or nitrogen. Moreover, degasification of electrodes, subsequent to their use in carbon monoxide discharge, was much more difficult than that of electrodes used in hydrogen or nitrogen.

No anode spots were formed in pure oxygen under any conditions. In mixtures of oxygen and carbon monoxide, spots did not form until the carbon monoxide content of the mixture had reached about 30 percent. Then anode spots which were characteristic of carbon monoxide were formed.

An electrode was "soaked" to saturation in carbon monoxide. The carbon monoxide was then removed from the tube and oxygen was substituted. Under these conditions, spots which were characteristic of carbon monoxide formed on the anode which was then full of carbon monoxide. Such spots

lasted for three or four minutes. This observation is direct proof that the anode spots are formed by gas being evolved from the anode under electron bombardment. The previous observation that 30 percent carbon monoxide in oxygen was necessary for anode spot formation precluded any possibility of the formation of these spots by any small amount of residual gas.

Anode spots were not formed in pure argon or pure neon. In these gases there was a tendency for the positive column to separate into two or more parts which rotated with respect to the axis of the tube. These streamers ended in bright spots on the anode which, however, were not of the same nature nor of the same origin as the anode spots now under investigation.

In argon, neon, and helium, the presence of mercury vapor given off from a mercury surface in the tube permitted the formation of bright anode spots. Bright anode spots also were formed when ten and five percent hydrogen was present in argon and neon respectively. Since no arrangement was made in the present apparatus for mixing and circulating the gases in the discharge tube, the above percentages may be somewhat in error. However, they are of the correct order of magnitude.

When the helium was apparently pure except for a small trace of hydrogen, very weak yellow anode spots appeared. These weak spots in helium were much larger than those for a corresponding pressure in another gas. However, these spots were symmetrically arranged and had all the characteristics of true anode spots. Bright anode spots appeared on the anode in a discharge in helium to which two tenths of one percent hydrogen had been added.

Effect of the metal of the electrodes. The effect of the metal on the formation of anode spots was studied only qualitatively. Anode spots formed on electrodes of iron, nickel, copper, aluminum, and brass. Electrodes of iron were used almost entirely for the quantitative study because its rate of sputtering was low. However, electrodes of nickel produced no noticeable change in the characteristics of the spots from those observed on iron electrodes. The thickness of the electrodes was found important only insofar as it affected the change of temperature of the electrodes.

The anode spots were not symmetrically arranged on the anode when impurities were present on the surface of the anode or when a new electrode was used as anode without previous degassing. However, the use of a new untreated electrode for a few minutes as cathode put it into such a condition that a symmetrical pattern of spots was formed when it was subsequently made anode.

The use of a barium coated electrode as cathode resulted in a decrease in the potential drop across the tube. As cathode it gave a symmetrical arrangement of spots on an uncoated electrode used as the anode; but when it was used as anode the spots were very unsymmetrically arranged, due most probably to the non-uniformity of the barium oxide layer.

Unsymmetrically arranged anode spots were formed on a carbon anode. The effects of local heating produced bright anode spots on the carbon. The carbon electrode could not be outgassed with the induction furnace. More-

over, the surface of the carbon could not be made to absorb gas uniformly by reversing the direction of the current because the discharge from the cathode was concentrated on several small areas on the carbon surface of the sleeve of this electrode. On the whole, the carbon electrode was unsatisfactory both as a cathode and as an anode. Nevertheless, anode spots were formed on its surface from the occluded gases.

Faint anode spots which were symmetrically arranged appeared on the surface of an anode of mercury in hydrogen and in the rare gases.

Rotation of the anode spots. The spots were seldom stationary on the anode for any length of time. Under the influence of the magnetic field which was set up by the passage of the current through the tube, the pattern of spots rotated with respect to the central axis of the tube, sometimes in a clockwise direction and at other times in a counter clockwise direction. The angular velocities of the spots in the various rings were not the same, the outer ring having the largest. At times the direction of rotation in two concentric rings was opposite. An increase in the distance between the electrodes increased the tendency for rotation of the pattern.

A solenoid placed coaxial with the tube, and away from the anode, so that a part of the field was radial to the electrode, could change the rotational velocity of the spots in the rings and even reverse the direction of rotation. When a solenoid was placed perpendicular to the axis of the tube in the immediate region of the anode, the configuration of spots was deformed by the magnetic forces so that the spots then appeared in a deformed circular pattern which also rotated rapidly during the application of the magnetic field of the solenoid. An unstable and unsymmetrical pattern of spots always formed when the walls of the tube in the neighborhood of the anode were badly sputtered.

Size and shape of electrodes. Circular electrodes of 41 mm and 34 mm in diameter were used. Under the same experimental conditions, the size of the spots was larger on the larger electrodes.

The use of a small spiral incandescent tungsten cathode did not destroy the symmetry of the anode pattern of spots when this cathode was placed on the line of the axis of the anode.

That the pattern of spots was governed primarily by the shape of the anode was proved by the use of a circular cathode and a triangular anode on which the spots formed in a triangular pattern which contained as many as four distinct triangles with their sides parallel to the edges of the anode. When the electrodes were placed so close that the form of the cathode influenced the field at the anode the spots on the anode were equally spaced on the sides of the triangles, but when the electrode separation was increased to some extent, the spots, except those forming the vertices of the triangles, tended to concentrate toward the middle of the sides of the triangles, but even then the form of the triangle was not destroyed.

When the electrodes were not parallel, an asymmetrical arrangement of spots always resulted. Under these conditions, the angular velocity of a spot was not uniform. Its angular velocity was greatest where the separation of the electrodes was greatest.

When the electrodes were parallel their centers were not on the same horizontal lines. The pattern of spots was displaced from one edge of the anode.

Size and intensity of anode spots. In general the size of the spots increased with an increase in the gas content and temperature of the electrode, with a decrease in the gas pressure, with an increase in the size of the electrode, and slightly with a decrease of the distance between the electrodes. The size of the spots definitely decreased with an increase in current and voltage. It also decreased with an increase in the age of the spots, although, for constant potential, the current decreased during their life.

Figure 3 is composed of two photographs of patterns of anode spots in hydrogen at 2.6 mm pressure and electrode separation of 17.2 cm. The pattern on the left was formed by 210 milliamperes at 1300 volts and the pattern



Fig. 3. Change of number of spots with change in current and voltage.

on the right by 30 milliamperes and 725 volts. These photographs show the change in the number and in the intensity of the spots with a change of current and voltage.

The change of the size of the spots with the change of temperature of the anode is shown in Figure 4. These photographs were taken as a discharge

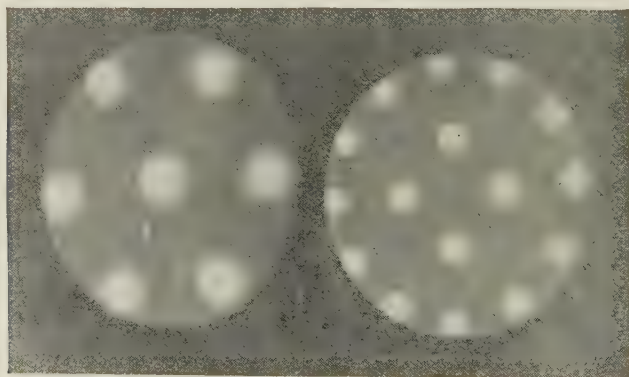


Fig. 4. Change in size and number of spots with change in temperature of anode.

passed through hydrogen at a pressure of 2.45 mm between electrodes separated 17.7 cm. The picture on the right is that of an anode which was saturated with gas by means of soaking it previously as cathode. This picture was taken after the electrode had cooled to room temperature, with a current of 115 milliamperes at 1120 volts. The picture on the left was taken while the anode was still red hot from its previous use as cathode, with a current of 115 milliamperes and 1100 volts.

The intensity of the spots increased with an increase in current and voltage. To a small degree, it depended on the kind of gas. Hydrogen gave brighter spots than nitrogen. The intensity was quite high when a rare gas was mixed with hydrogen or mercury vapor.

Factors which influence the number of spots. The number of spots which appeared in the pattern on the anode increased with an increase of pressure, with an increase in current, with an increase in the amount of gas in the surface of the anode up to a saturation value, and slightly with an increase of distance between the electrodes. An example of the increase in the number of spots with an increase in current and voltage is given in Figure 3 above. The number of spots decreased with an increase of the temperature of the anode within certain limits. An example is given in Figure 4.

The same pattern of spots was obtained after a thirty second period of soaking of the electrode as when the electrode was soaked ten minutes provided that the temperature change in the electrode during this latter period was not over two hundred degrees. This indicates that the condition of the surface layer or near surface layer governed the number of spots and that this layer quickly reached saturation.

Mention has already been made of the observation that spots were formed from gas which was absorbed by mere contact with the metal. The following experiment showed that spots were also formed by gas which diffused to the surface of the anode. The cathode was soaked with hydrogen gas until saturation was reached, then it was used as anode until the spots disappeared. Immediately afterward the tube was evacuated to a pressure less than 2×10^{-4} mm at which pressure it remained for forty-eight hours. At the end of this period, hydrogen was again passed into the tube until a pressure of 3.3 mm was reached. Forty spots in four rings were present when the discharge was established within a few seconds after the gas was admitted. At the end of 25 seconds the number of spots had decreased to 30 in three rings. The remainder of the spots disappeared simultaneously at 30 seconds.

The large number of spots which appeared under the above conditions and the short life of the spots indicate that the gas, which had penetrated to a considerable depth in the electrode diffused to the surface or to the layers immediately underneath the surface. Since a considerable amount of gas was given off from the anode only during a thirty second period, one may conclude that the gas which diffused to the surface, was held there

by the molecular forces of the metal. Since no similar effect was observed when a degassed electrode was treated in a similar manner, it is not probable that these spots were formed from hydrogen absorbed while the electrodes were subjected to the low gas pressure given above.

Application of the phenomenon of anode spots to the study of the rates of absorption and emission of gases by the electrodes of a Geissler discharge: Let us assume that the cathode of a direct current Geissler discharge absorbs gas under the influence of positive ion bombardment at a rate which is a function of the number and energy of the positive ions which strike and of the gas content of the cathode at that particular moment. Let us further assume that the anode emits its absorbed gas under the influence of electron bombardment at a rate which is a function of the velocity of the electrons at the moment of striking, of the number striking, of the gas content of the anode, and of the kind of gas.

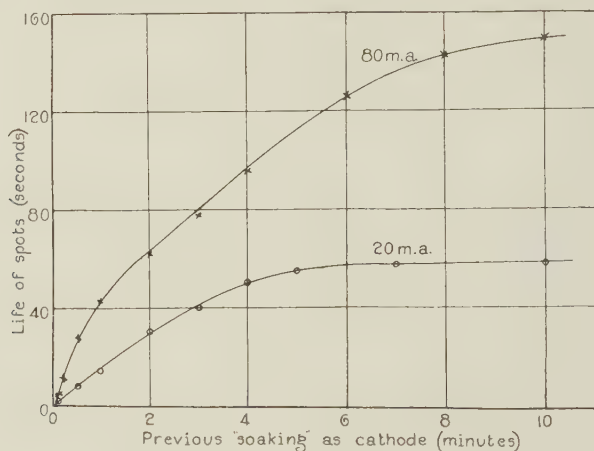


Fig. 5. Life-soaking curves for different soaking currents.

In order to test the validity of the above assumptions a series of experiments was carried out in hydrogen. Typical results are given in Fig. 5. The lower curve was obtained by subjecting the cathode to soaking in 3mm of hydrogen with a current of 20 milliamperes for different periods. At the end of each of these periods of soaking, the direction of the discharge was reversed and a current of 110 milliamperes was passed through the discharge until the last spot had disappeared from the anode. The lower curve of Figure 5 shows that, with a soaking current of 20 milliamperes, the life of the spots approached a constant value with a soaking period of 5 minutes. However, when a soaking current of 80 milliamperes was used the life of the spots was relatively longer as shown in the upper curve.

We believe that the differences in the lives of the spots for different soaking currents were due to differences in the rates of the absorption and in the total amount of gas absorbed. This difference in absorption was due to the difference in the temperature of the cathode during positive ion bombardment

and to the difference in the energy of the impinging positive ions under the two conditions.

Many similar curves were obtained in hydrogen with both the small and the large experimental tubes. The rates of absorption and emission of hydrogen changed with the change of conditions in the electrode. However, for a series of runs on the same day, the same type of curves was obtained. It was not possible to retrace the curves backwards because of a change in the temperature of the electrode in the long periods of soaking. For soaking currents between 20 and 80 milliamperes the curves fell between those given in Figure 5.

Since the charge on the walls of the tube influences the electric field at the anode and since the ratio of the random current to the drift current in the tube governs the anode drop, it was deemed advisable to investigate the effect of the diameter of the tube on the anode spots. To this end a tube of 10 cm was substituted for the tube of 6 cm diameter. The use of the larger tube resulted in a greater stability and uniformity of the pattern of the spots, less rotation of the spots and a longer period of use before cleaning was necessary. However, no appreciable difference appeared in the life-soaking curves which were obtained from the different tubes when the walls of the tubes were equally free from sputtered material. It was to be expected that a greater electrode separation would be required for the larger tube, because the length of the negative glow increase with an increase in the diameter of the tube.

It was possible to obtain curves as those given in Figure 5 only in hydrogen because in all gases having a strong positive column the change in the potential drop across the tube with the change in the gas content of the electrodes altered the position of the beginning of the positive column to such an extent that the anode was soon out of the narrow region in which the formation of anode spots was possible. However, in the case of carbon monoxide gas, the anode was moved through a small distance in order to keep it in the region of the anode spots. This method showed that the life of the spots for carbon monoxide, for a given amount of soaking, was considerably longer than that of hydrogen for similar soaking. This observation is only qualitative because the potential drop across the tube changed with the change in the distance of electrode separation.

Figure 6 contains the life-soaking curves for the same electrodes under the same conditions except that the curves were taken on consecutive days in the order given in the figure. Curve I, was obtained with new electrodes which had been carefully degassed by heating in vacuo by means of the induction furnace. Between the time of obtaining curves I and II, a discharge was maintained in the tube for short periods which totaled four hours after which the electrodes were again degassed by heating in vacuo. A similar procedure took place between the time of taking the data given in the consecutive curves of Figure 6. These curves show that the life of the spots increased with the use of and the degassing of the electrodes. On the assumption that a certain rate of evolution of gas from the anode is neces-

sary for the formation of anode spots, these curves show that the anode evolves gas for a longer time above that rate when the electrode is used in a discharge and is subsequently degassed.

In order than an electrode, under constant current conditions, evolve gas above a certain rate for a longer period, it must contain a greater amount of

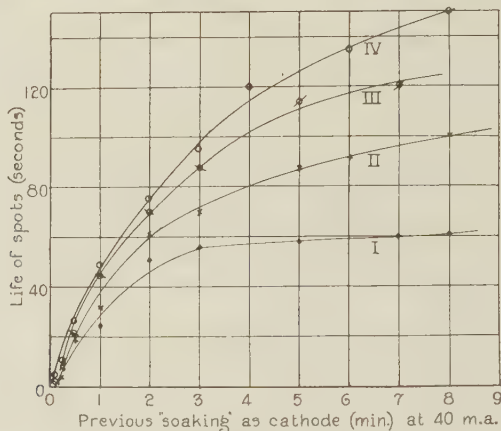


Fig. 6. Life-soaking curves showing effect of aging of electrode.

gas to begin with or the rate of evolution of gas must be more gradual or both conditions must be fulfilled. For this we give the following explanation.

It is certain that some of the gas ions which are driven into the anode structure by considerable electrical force are more difficult to remove than are the molecules of the original occluded gas. Hence, degassing by means of heating

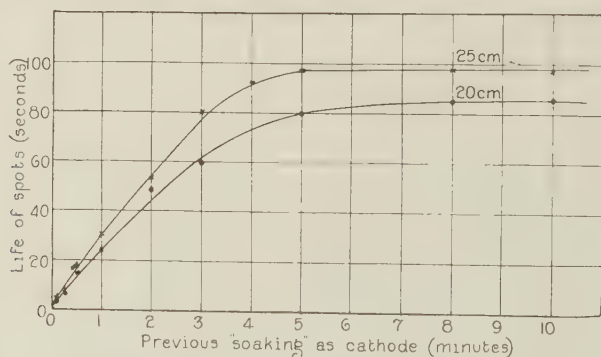


Fig. 7. Life-soaking curves for different electrode separations.

in vacuo may not be so efficient in removing such gas molecules. Therefore, the electrode may contain more gas to begin with even after the same period of degassing than it did before it was used so much as cathode. On the other hand, the spacing of the molecules of the metal may be so changed by use and subsequent degassing, that the hydrogen molecules will then be absorbed more readily as they strike the cathode in the form of positive ions. Also they may penetrate deeper into the metal of the cathode.

Experimental evidence, which supports this hypothesis, is given by Yamada⁵ who found that absorption of hydrogen in palladium resulted in a uniform expansion in the space lattices and by Baum⁶ who found that hydrogen ions under the influence of 3000 volts not only penetrated a silver cathode to some distance but that they also produced fissures in the crystal structure of the metallic electrode.

The life soaking curves which are presented in Figure 7 were obtained from data in which the experimental conditions except the change in electrode separation were kept constant, as nearly as possible. These curves show that the life of the spots increases with an increase in the electrode separation. This increase of the life of the spots with increase of electrode separation was not due to temperature increase or aging effect of electrodes because the data for the curve at 20 cm were obtained immediately after that used in the curve at 25 cm.

Since the electrode contained approximately the same amount of gas in both cases at the end of similar periods of soaking, and since the number of electrons striking the anode was also the same, this difference in the life of the spots for different electrode separations must have been due primarily to a difference in the velocity of the electrons at impact on the anode by which the rate of evolution of gas would have been different.

This change in the velocity of impinging electrons could have been produced by a difference in the electric field depending on the position of the anode especially if it was placed near the beginning of the positive column. Moreover, a change in the anode drop of potential may produce a greater change in the energy of impact of an electron on the anode than that which corresponds to a change of V in the relation $eV = 1/2 mv^2$. For instance, if the anode drop of potential is just greater than the ionizing potential of the gas, some of the electrons will make ionizing collisions with the gas molecules in the region of anode space charge, and will thus lose most of their energy. Such electrons will then strike the anode with much less energy than that of the electrons which make only elastic collisions with molecules because their velocities are below that which corresponds to the velocities necessary for ionization or excitation of the gas molecule.

Change of potential with the change in the gas content of the electrode. In Figure 8 are given the time-voltage curves during the life of the anode spots for a constant current of 110 milliamperes in hydrogen at 3 mm pressure and electrode separation of 22 cm. The anode in the discharge from which the data for these curves were taken was soaked at 40 milliamperes for the different periods given in this figure. These curves show that the anode spots disappeared in each case at approximately the same voltage. When the experiment was continued beyond the time of the disappearance of the spots the potential drop approached a constant value of which there is some evidence in these curves. (The curves in the Figure 9 show this more plainly.) We believe that the constant potential drop was determined by the conditions in the tube reaching a state of equilibrium, that is, the change in the gas content of the electrodes must have reached a steady state. These curves

also show that, at least within given limits, the potential drop, immediately after the initiation of the discharge was lowered by an increase in the soaking period of the cathode. Each of these curves corresponds to the determination of one point of the life-soaking curve such as given in Figure 6.

The differences in the potential drop for the discharge as shown in these curves were due almost entirely to different amounts of gas in the electrodes. Different amounts of gas were obtained in each electrode by varying the time of reversal of the current during which the cathode absorbed gas and the anode emitted gas. Degassing the cathode by means of an induction furnace resulted in a lower maintaining potential at the beginning than that given in curve VI of Figure 8.

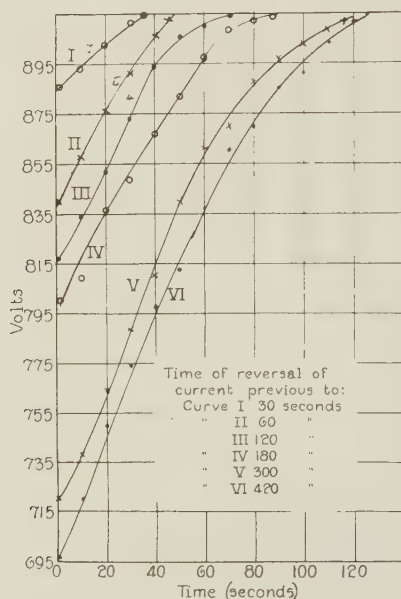


Fig. 8. Time-voltage curves during life of spots.

That the differences in the maintaining potential which are evident in the several curves and in each single curve at different times, were due almost wholly to the processes at the cathode was proved by the following experiment. Two new iron electrodes *A* and *B* were degassed in vacuo by an induction furnace to an equal degree. Then electrode *A* was made cathode and electrode *B* anode in a discharge of 100 milliamperes in hydrogen at 2.8 mm pressure. The variation of the voltage with time is given in curve I, Figure 9.

Since both electrodes were degassed to begin with most of the change in potential difference was due to absorption of gas at the cathode since electron bombardment could free few gas molecules from the already degassed anode.

Upon reversal of the direction of the discharge at the end of three minutes, results were almost identical with those given in curve I although in this case

the cathode was a degassed electrode but the anode contained gas as a result of previous use as cathode for three minutes. Thus we found that degassed cathode and anode produced the same time voltage characteristics as a degassed cathode and a gas filled anode. From this we conclude that the evolution of gas from an anode under electron bombardment has little or no effect on the potential drop of the discharge.

Subsequently, electrode *A* which contained some gas was made cathode and the results given in curve II of Figure 9 were obtained. The main difference in the curves I and II is a higher starting potential difference when the cathode contained some gas. The irregularity of curve I between 60 and 100 seconds is typical of the curves obtained with new electrodes which were degassed by the induction furnace. We believe the change in potential to

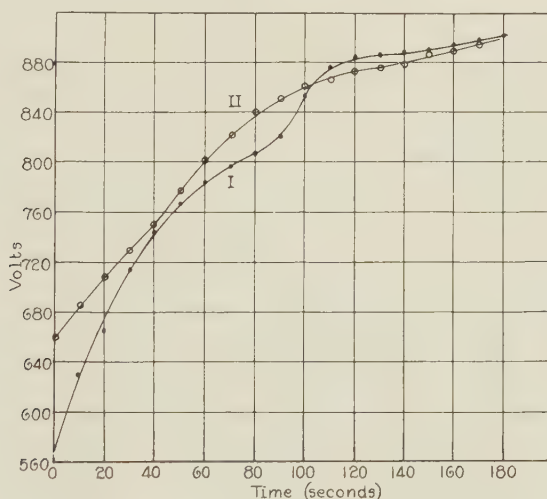


Fig. 9. Time-voltage curves with new electrodes.

be due to evaporation of impurities from the surface of the cathode, impurities which were brought to the surface of the metal during the first heat treatment.

DISCUSSION OF RESULTS

Summing up the behavior of the anode spots, we see that their formation and existence must depend on the joint action between the gases released from the anode and the electron stream to the anode. From their magnetic behavior and from their dependence on the distance between the electrodes, we deduce that they must be the manifestations of a splitting up of the electronic current into discrete and more or less stable "rays" or current-beams. Also, since their life was, within limits, proportional to the length of time the electrode had previously been used as cathode, since their number decreased with the time that the electrode was used as anode, since no spots formed on a well outgassed anode, and since spots having the color characteristic of carbon monoxide formed in a discharge in oxygen on an anode previously

soaked in carbon monoxide, we infer that gas must escape from the anode in order that the formation of electron beams and their resultant anode spots be possible.

On the assumption that one necessary condition for the formation of anode spots is the evolution of a certain amount of gas from the surface of the anode when it is subjected to electron bombardment, we shall now give an explanation of the formation of the anode spots.

When no gas is liberated by the anode, the electrons form a space charge sheath which limits the more intense part of the field to within a short distance of the anode,⁹ of the order of a few millimeters at the pressure used. Outside the sheath the electric intensity is so small that the drift velocity of the electrons due to the field is not sufficient to keep them in relatively straight paths parallel to the axis of the tube, and they scatter by successive collisions with the gas molecules until the slowly drifting stream fills the cross section of the tube.

When these electrons enter the sheath, their increased speed causes them to fall to the anode in nearly straight lines. It is, then, in this sheath, where the field is large, that there is any possibility of formation of electron beams; and the chance of their formation increases as the sheath increases in thickness.

If, now, gas is emitted from the anode, the molecules will either already be ions, or will soon become ions by collision with electrons, and these ions will partially neutralize the electronic space charge, thus increasing the sheath thickness and decreasing slightly the anode fall of potential, and therefore making the formation of beams more probable. Inasmuch as one positive hydrogen molecular ion neutralizes the space charge of three hundred or more electrons a small quantity of gas from the anode will cause a large change in sheath thickness, and under these conditions the electrons will move in straight paths for a centimeter or more before striking the anode.

Only a small portion of the current will be concentrated in the spots, for the gas will scatter many electrons to the other parts of the anode. These rays will be the favored paths, however, and the fastest electrons, those which have suffered few collisions, will travel therein. These faster electrons will create more ions than the other scattered ones, and so, a short time after the discharge is started, these beams will act as separate phenomena superimposed on the back-ground of scattered electrons, having their own potential distribution, their own motions, and their constant current density. This current is probably due predominantly to the ions created by the original electron beam in the gas coming from the anode. For this reason, and because the gas from the anode increases the sheath thickness, it is probable that the number of spots or beams present is proportional to the amount of gas evolved by the anode.

Since anode spots form only at the beginning of the positive column in gases which have a strong positive column and since they form before the first striation and in each dark space between successive striations when

⁹ Langmuir, *Gen. Elec. Rev.* **27**, 767 (1924).

striations occur in the tube, it is now necessary to show why the spots form on the anode when it is placed in these positions.

Langmuir⁹ explains how an electron sheath around an anode may be broken down suddenly, through its neutralization by positive ions which are formed in the space charge sheath, to such an extent that the anode drop falls discontinuously to a lower value. He found that, when breakdown occurred, the anode glow usually appeared in the form of a sharply defined hemispherical region several times more luminous than the surrounding region. In this explanation, he assumes that very few gas molecules are present in the electron space charge sheath so that only a small fraction of the electrons which pass through this sheath make ionizing collisions. He further assumes that the gas molecules which are present in this sheath come into the sheath from the region on the outside of the anode sheath. *

However, it is apparent from his theory that the breakdown of the electron sheath will be brought about the more easily the greater the concentration of gas molecules in the space charge sheath since a larger percentage of the electrons then make ionizing collisions with the gas molecules in their passage through the space charge sheath. Thus we see that the emission of gas from the anode will assist in the neutralization of the space charge sheath, which results in an increase in its thickness and a decrease in the total anode drop of potential.

It is evident from the preceding discussion that the electron space charge sheath will increase in thickness or breakdown (in the sense as used by Langmuir) more easily in the regions where the field is small. Therefore, the anode spots, whose appearance is due to the increase in the thickness of the electron space charge sheath of the anode or to its breakdown, will form when the anode is placed in the region at the beginning of the positive column where the electric field has not yet attained the maximum value of the positive column. In the dark space regions between striations, the field is again small. Therefore, these dark space regions between striations will also be favored regions for the formation of anode spots.

A field which is below that necessary for the production of an anode glow by ionization is excluded from this consideration. Consequently, the region of the Faraday dark space is excluded because there the anode drop of potential is too low to produce ionization, so that one would not expect the formation of anode spots.

We believe that anode spots do not form in oxygen because the oxygen ions, on striking the cathode, react with the metal of the cathode to form stable compounds which are not decomposed under subsequent electron bombardment of the anode.

Since the rare gases, helium, neon, and argon do not react chemically with any substance under any condition, and since very little gas was evolved in the degasification of electrodes subsequent to their use in these rare gases, we infer that these gases are not absorbed by the metal of the electrodes in amounts which are capable of producing anode spots. We believe that very weak yellow anode spots were formed in helium which contained a trace of

hydrogen whose presence could be detected by means of a direct vision spectroscope because the anode space charge sheath was not sufficiently broken down by the presence of a few hydrogen ions to permit the formation of bright spots.

Considering the effects of absorption of hydrogen by an electrode in a mixture with the rare gases and the production of hydrogen ions by collision with excited atoms, we have been able to explain, to our own satisfaction, the formation of bright anode spots when 10 percent, 5 percent and two tenths of one percent of hydrogen is present in argon, neon and helium, respectively.

When mercury is present in the discharge tube, sufficient mercury molecules are present on the surface of the anode to bring about the formation of anode spots in each of the rare gases. Anode spots appeared under similar conditions of the gas as those described by MacKay⁸ who photographed the spots in a discharge in helium containing mercury vapor. MacKay reports in the same paper the formation of spots of similar nature when mercury was excluded from the discharge tube. In that event, the helium which he used must have had, as impurity, hydrogen to the extent about two tenths of one percent. From the nature of the spots formed when a trace of hydrogen was present in the helium, it is doubtful if anode spots will be formed at all in pure helium.

Since anodes spots are formed by beams of electrons we would expect these beams to be influenced or even rotated by the application of a suitable external magnetic field. We offer the following explanation for their rotation in the absence of a magnetic field.

The drift current approaches the anode in the form of a frustrum of a cone rather than in the form of a cylinder so that there will be present in the tube a small resultant radial magnetic field which will be sufficient under certain conditions to set the whole pattern in rotation. As the electrodes are separated farther apart, the influence of the electrodes on the drift current will be less, so that some of the drift current will approach the anode at a greater angle with the axis of the tube in a manner which may be likened to the change of the lines of electric force. Then the radial component of the magnetic field will be greater so that the angular velocity of the pattern will be increased.

In order to explain the change of sense of rotation of the pattern, the rotation in the opposite sense in consecutive rings and even the formation of a stable pattern, one would have to consider, in addition to the component of the magnetic field already discussed, the magnetic field set up by the diffusion of the electrons to the walls.

Since a given rate of emission of gases from the anode is necessary for the formation of anode spots, this phenomenon can be used as a measure of the rate of emission of gas from the anode and indirectly as a measure of gas absorption by the cathode. By the application of this method, we find that a cathode absorbs certain gases in proportion to the time of soaking up to a certain saturation value which is determined by the current and voltage of soaking, the temperature of the cathode and the previous treatment of the

electrode. We also find that the anode emits both absorbed and original occluded gas when it is subjected to electron bombardment.

Finally, in consideration of the evidence which follows, we believe that the absorption of hydrogen gas by the cathode of a Geissler discharge increases the potential drop across the tube until saturation of the cathode with gas is reached.

1. The potential drop increased with time until it reached approximately a constant value which depended upon the current density and the temperature of the cathode, in almost the same way that the life of the anode spots increased with an increase in the period of soaking of the cathode for a similar current density.

2. Degassing an electrode previous to its use as cathode either by having it serve as anode in a Geissler discharge or by heating it in *vacuo* with induction currents resulted in a decrease in the potential necessary to maintain the discharge for a short time after the discharge had struck. This decrease was a function of the amount of gas which had been emitted from the electrode in degassing.

3. After a discharge had been discontinued for a time, the potential drop was always lower at the second initiation of the discharge than it was just previous to the time of its discontinuation.

4. Although the cathode contained different amounts of gas to begin with in different experiments under the same conditions, the potential drop approached the same limit in each case as the cathode approached saturation in absorption of gas.

5. Experiments under identical conditions, except that in one case the anode was full of gas and in the other it was thoroughly degassed, gave almost identical time voltage curves. This we take to be good evidence that the emission of gas from the anode has little or no effect on the potential drop of a discharge.

We wish to express our indebtedness to L. B. Headrick and Dr. P. M. Morse for helpful suggestions in this work.

